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Bernstein et al.

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[45] **Date of Patent: Nov. 1, 1988**

[54] **INFRARED MOLECULAR SPECIES MONITOR**

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[73] Assignee: **Spectral Sciences, Inc.,** Burlington, Mass.

[21] Appl. No.: **909,918**

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[51] **Int. Cl.**[4] **G01N 21/61**

[52] **U.S. Cl.** **250/343;** 250/339

[58] **Field of Search** 250/493.1, 345, 343, 250/339

[56] **References Cited**

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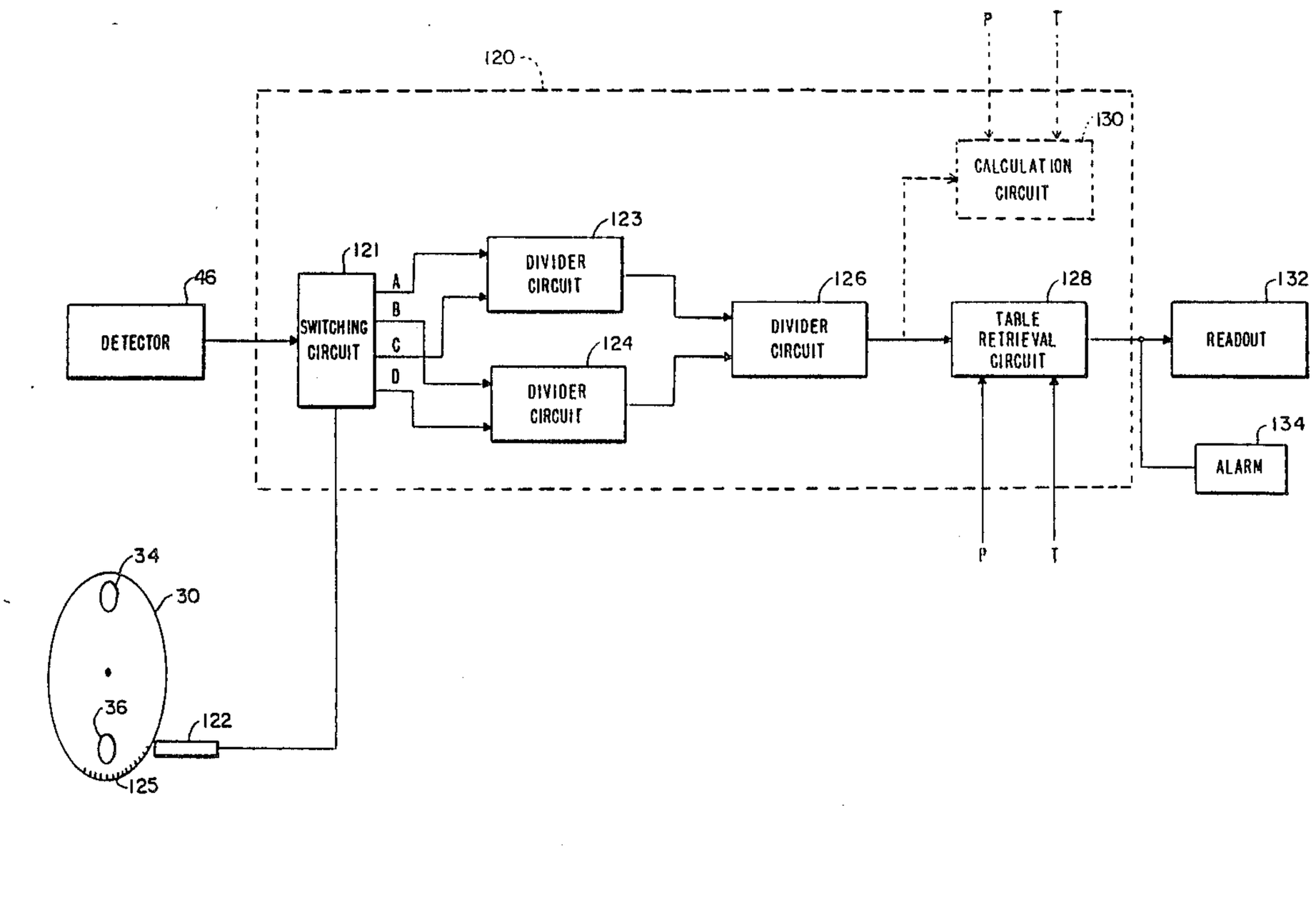
Primary Examiner—Carolyn E. Fields
Attorney, Agent, or Firm—Joseph S. Iandiorio; Brian M. Dingman

[57] **ABSTRACT**

An infrared monitor for measuring the presence of at least one gas phase molecular species including a sample path for containing a sample to be monitored for the molecular species. A sample beam of infrared source emission of the molecular species to be monitored for passage through the sample path is provided to the sample path. The sample beam includes at least one primary spectral emission line which is significantly absorbed by the molecular species. The decrease in the intensity of the at least one primary infrared source spectral emission line passing through the sample path is detected as a function of the absorption of the at least one line by the molecular species present in the sample.

11 Claims, 10 Drawing Sheets



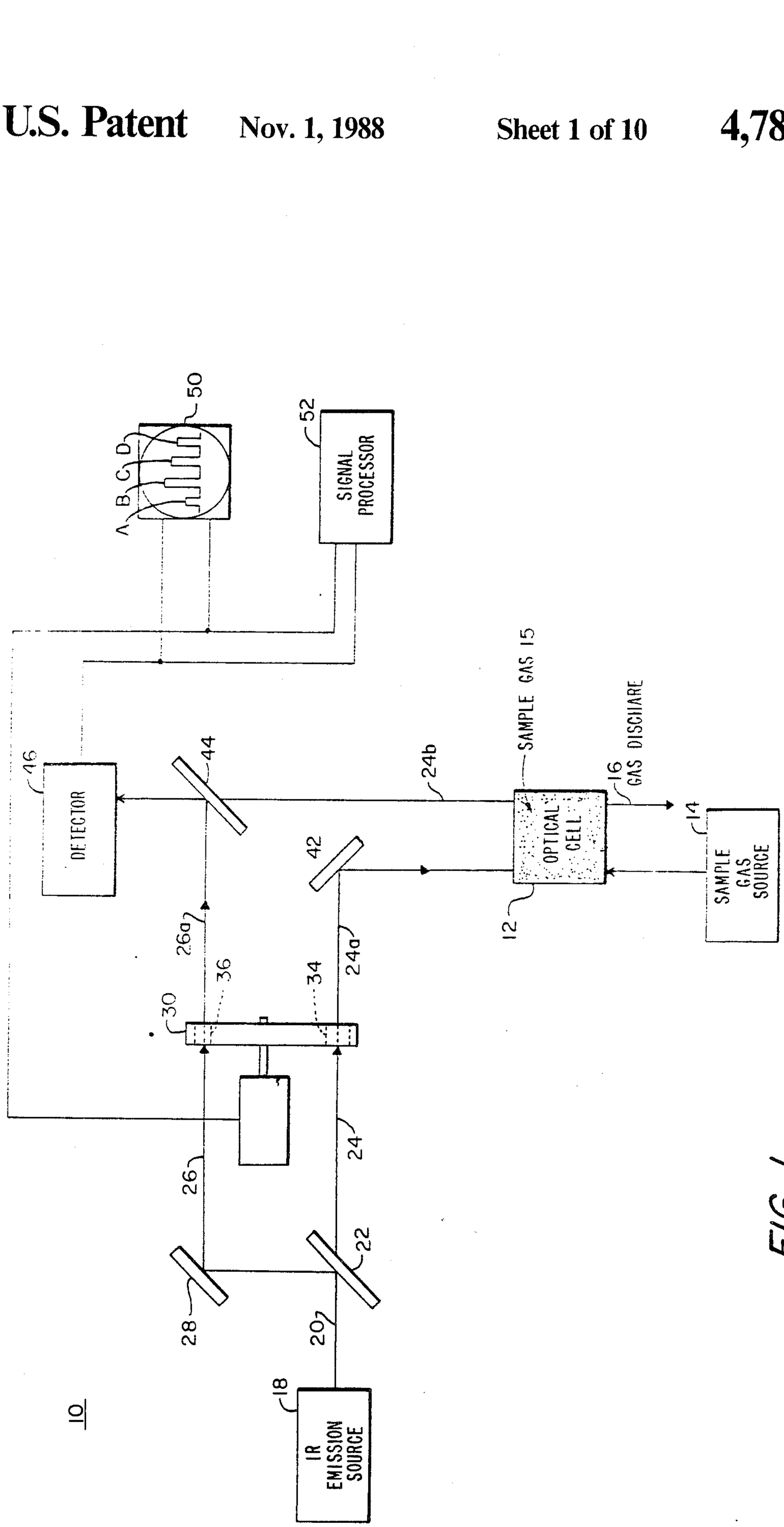

10
IR EMISSION SOURCE
18
20
22
24
24a
24b
26
26a
28
30
34
36
42
44
DETECTOR
16
SIGNAL PROCESSOR
52
A
B
C
D
50
SAMPLE GAS 15
OPTICAL CELL
12
16
GAS DISCHARE
14
SAMPLE GAS SOURCE

FIG. 1

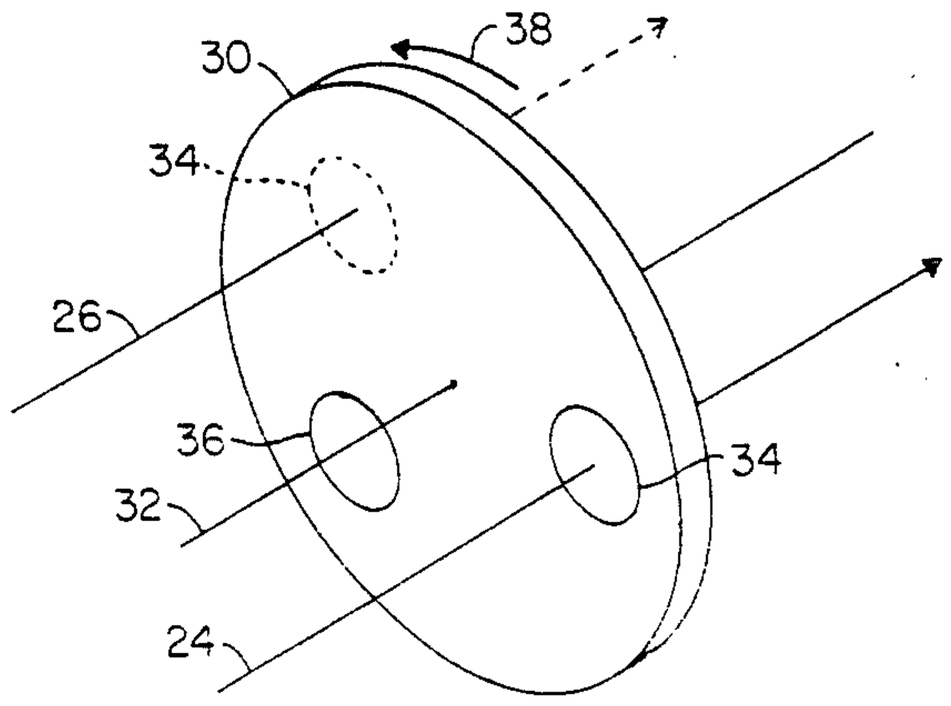

30
38
34
26
36
32
24
34

FIG. 2

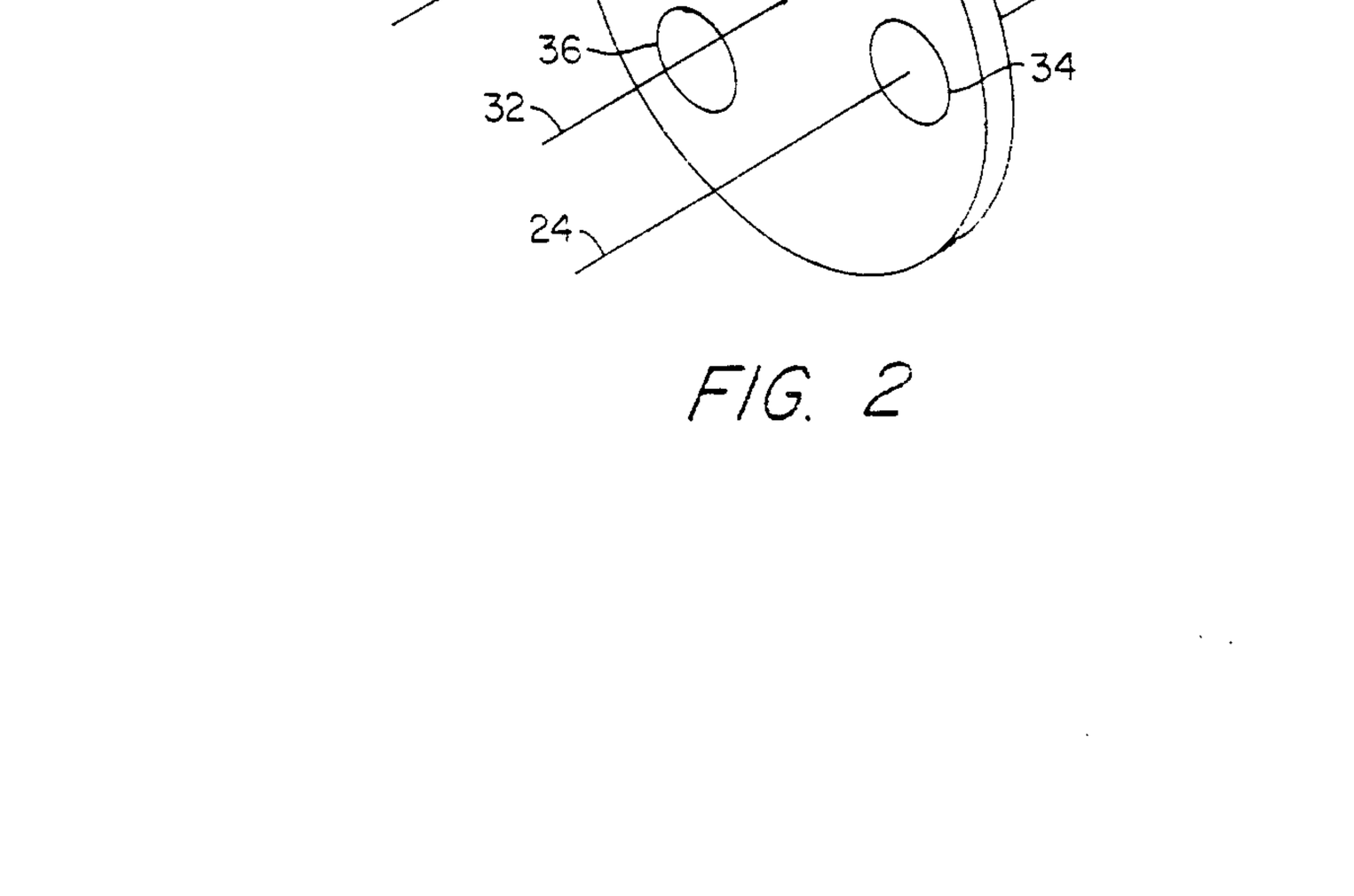

INTENSITY
A
B
C
D
0
CHOPPER WHEEL ROTATION (DEGREES)

FIG. 3

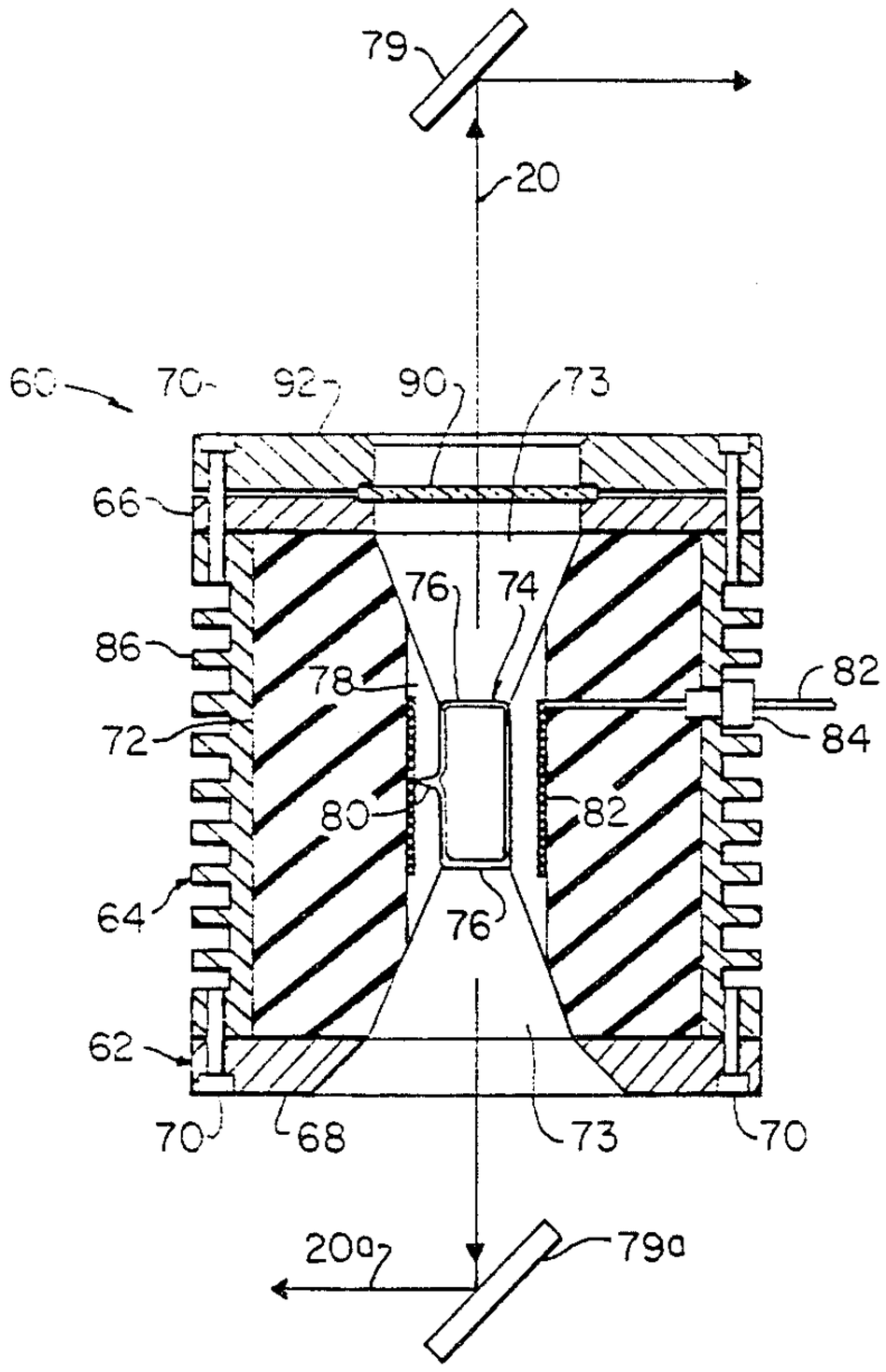

79
20
60
70
92
90
73
66
76
74
86
78
82
72
84
80
82
64
76
62
70
68
73
70
20a
79a

FIG. 4

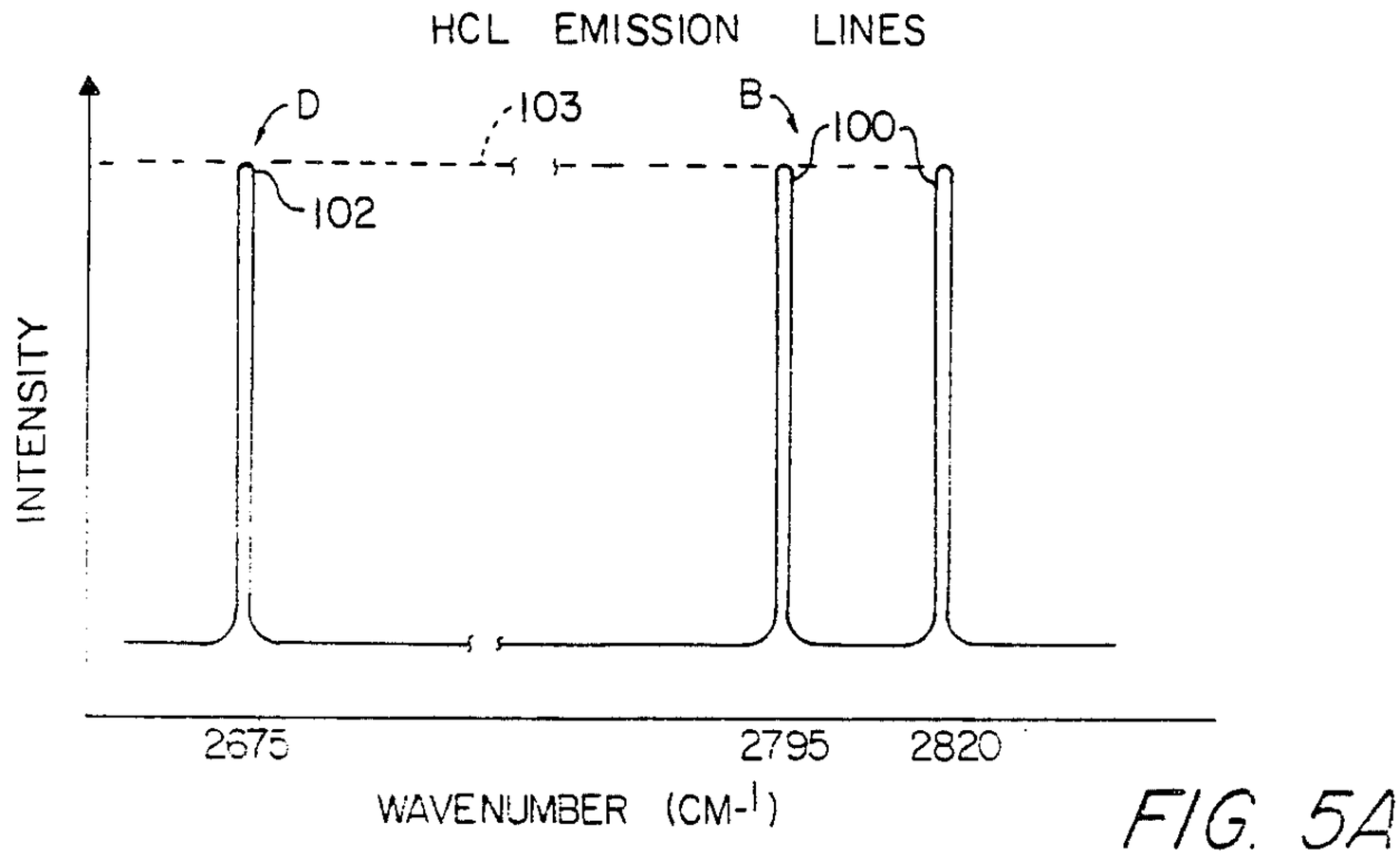


FIG. 5A

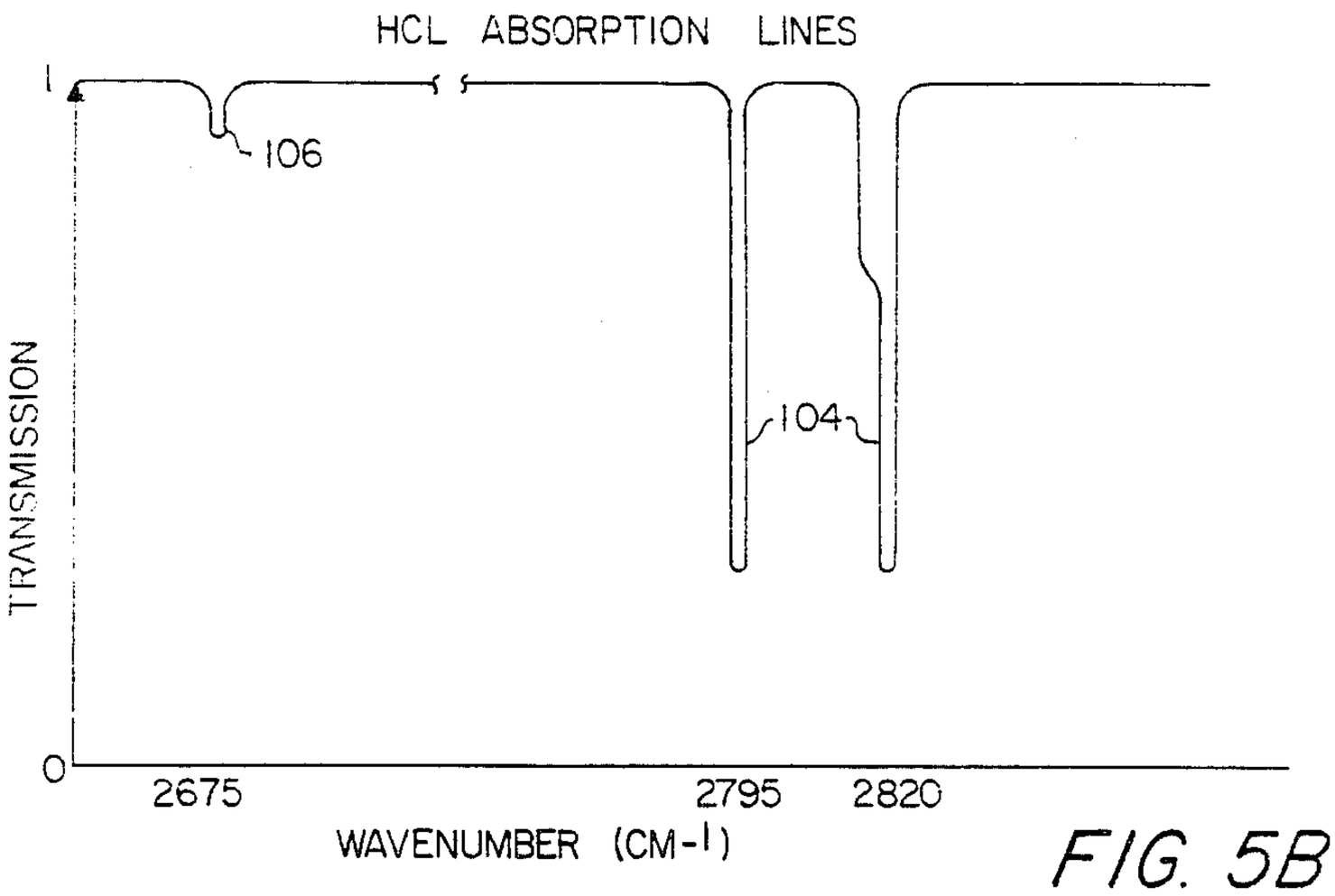


FIG. 5B

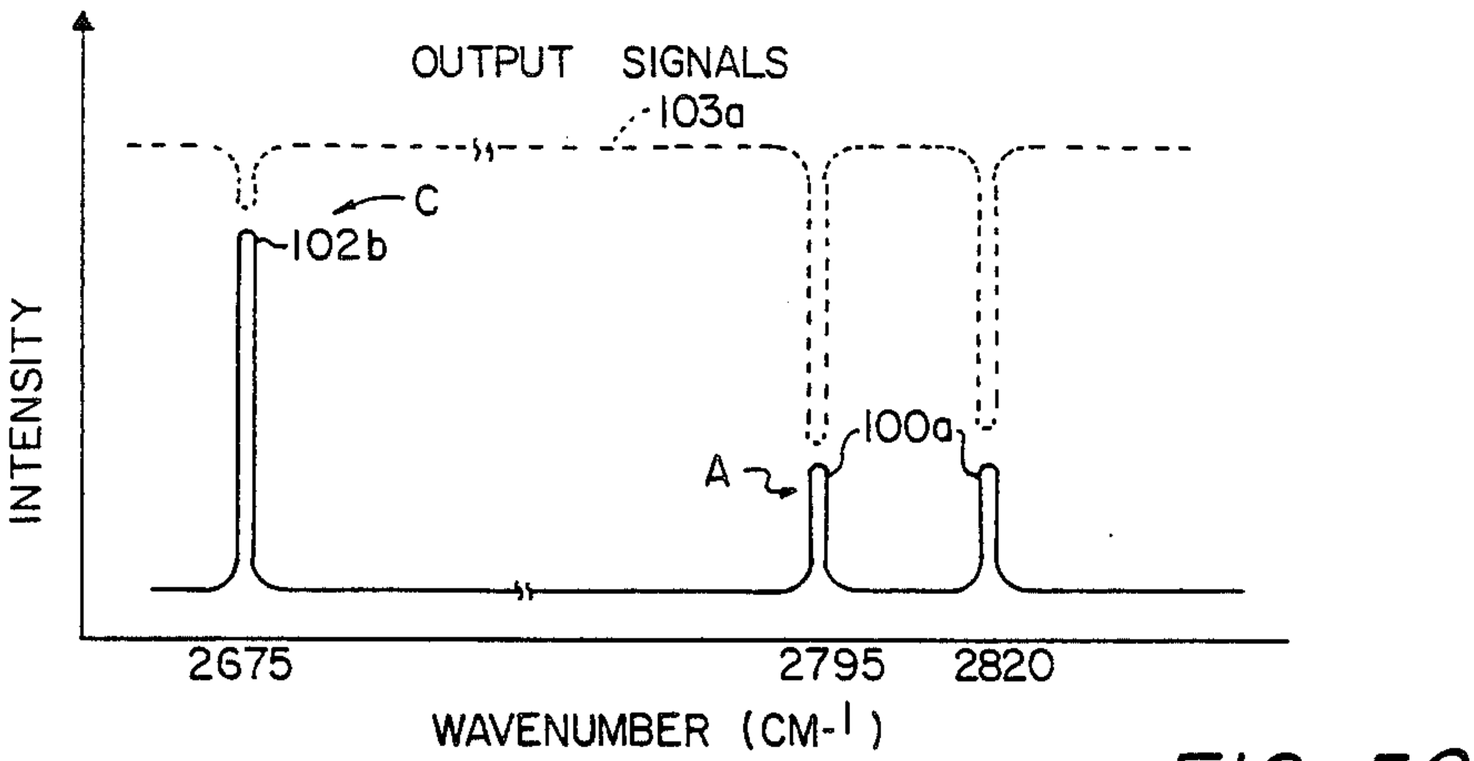


FIG. 5C

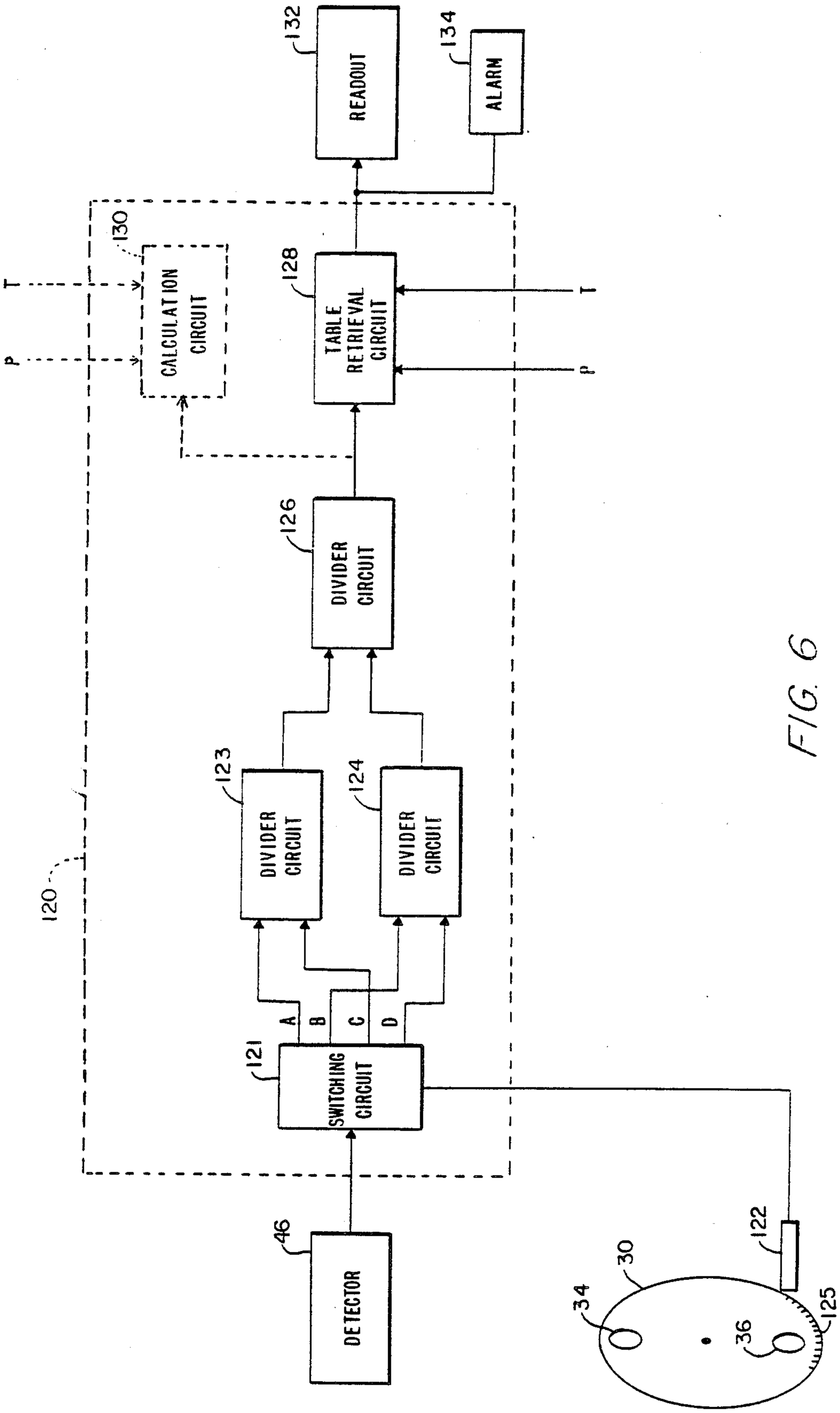

132
READOUT
134
ALARM
130
CALCULATION CIRCUIT
T
P
128
TABLE RETRIEVAL CIRCUIT
T
P
126
DIVIDER CIRCUIT
123
DIVIDER CIRCUIT
124
DIVIDER CIRCUIT
A
B
C
D
121
SWITCHING CIRCUIT
120
46
DETECTOR
122
30
34
36
125

FIG. 6

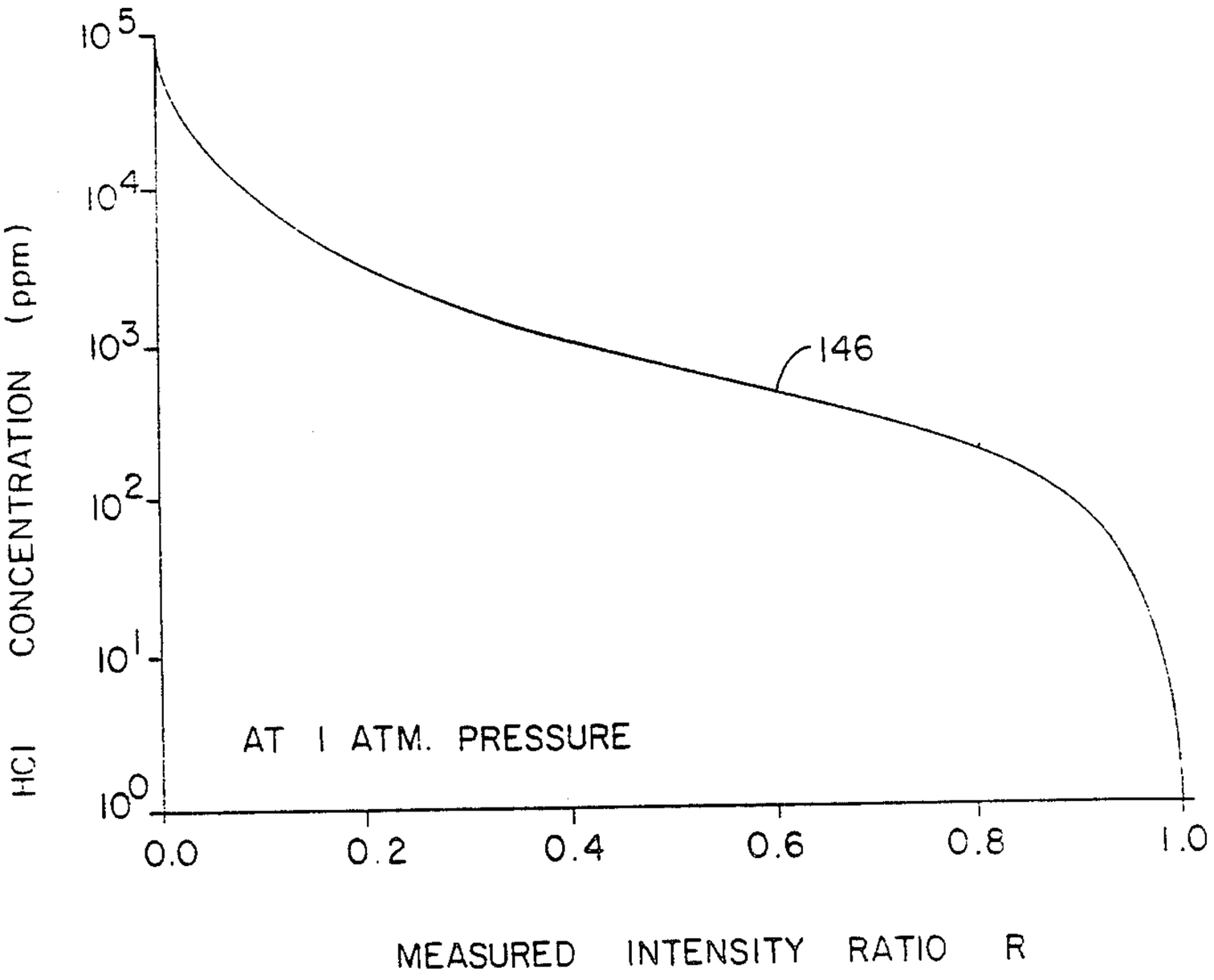

HCl CONCENTRATION (ppm)
10^5
10^4
10^3
10^2
10^1
10^0
146
AT 1 ATM. PRESSURE
0.0
0.2
0.4
0.6
0.8
1.0
MEASURED INTENSITY RATIO R

FIG. 7

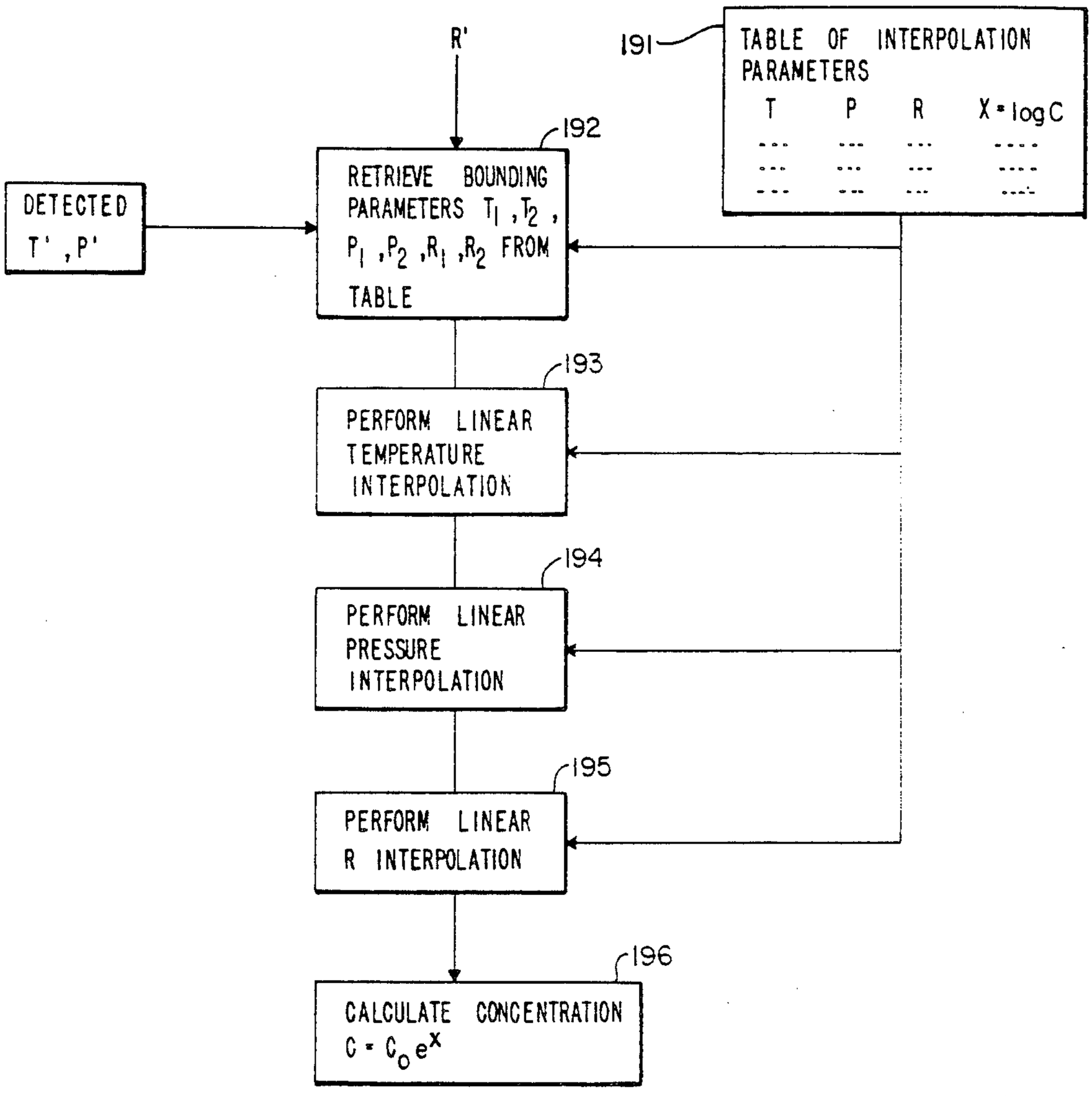

R'
191
TABLE OF INTERPOLATION PARAMETERS
T P R X = log C
192
RETRIEVE BOUNDING PARAMETERS T_1, T_2, P_1, P_2, R_1, R_2 FROM TABLE
DETECTED T', P'
193
PERFORM LINEAR TEMPERATURE INTERPOLATION
194
PERFORM LINEAR PRESSURE INTERPOLATION
195
PERFORM LINEAR R INTERPOLATION
196
CALCULATE CONCENTRATION $C = C_0 e^X$

FIG. 8

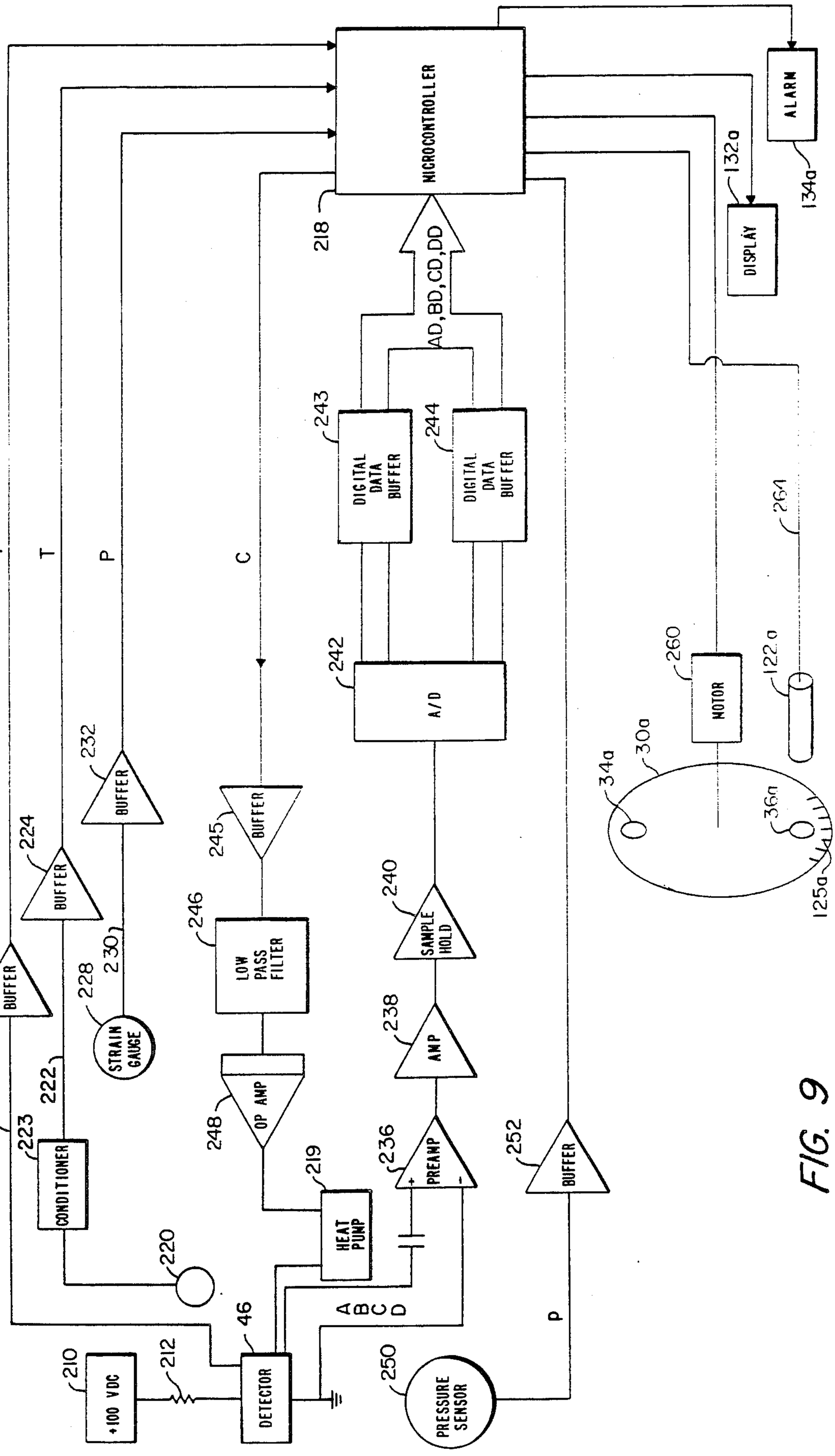

MICROCONTROLLER
ALARM
DISPLAY
132a
134a
218
AD,BD,CD,DD
243
244
DIGITAL DATA BUFFER
DIGITAL DATA BUFFER
242
A/D
240
SAMPLE HOLD
238
AMP
236
PREAMP
+
-
252
BUFFER
t
T
P
C
216
BUFFER
224
BUFFER
232
BUFFER
228
STRAIN GAUGE
230
222
214
223
CONDITIONER
220
246
LOW PASS FILTER
245
BUFFER
248
OP AMP
219
HEAT PUMP
A
B
C
D
46
210
+100 VDC
212
DETECTOR
250
PRESSURE SENSOR
P
261
260
MOTOR
122a
30a
34a
36a
125a

FIG. 9

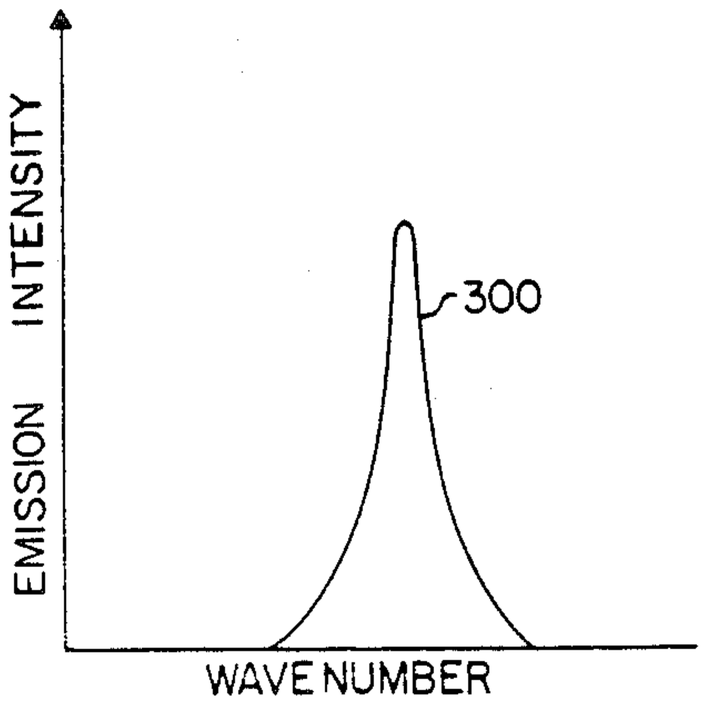


FIG. 10A

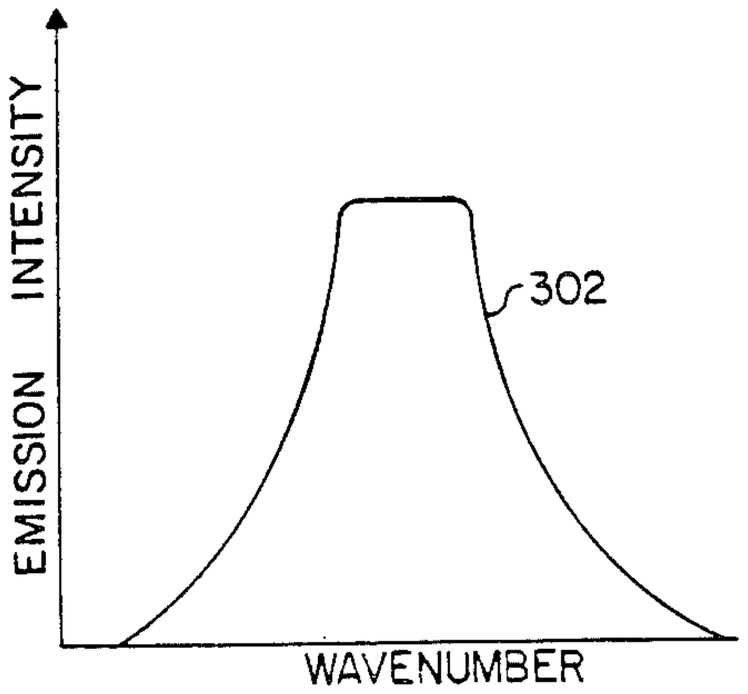


FIG. 10B

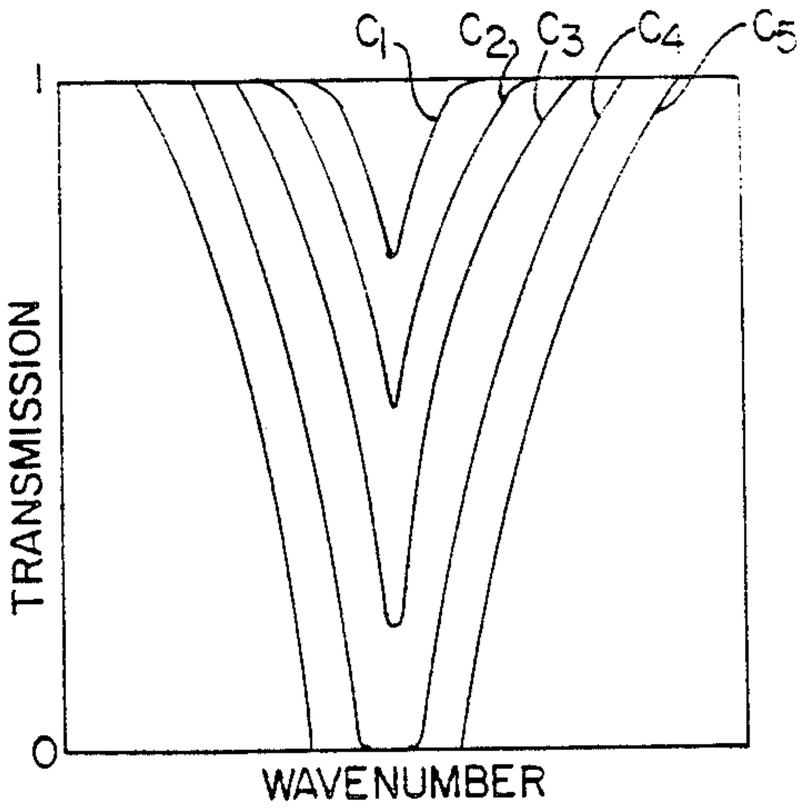


FIG. 10C

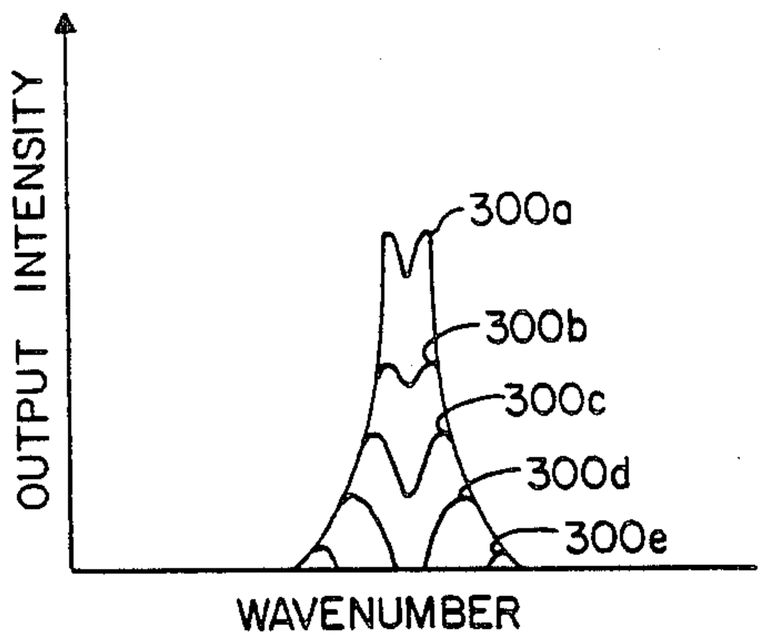


FIG. 10D

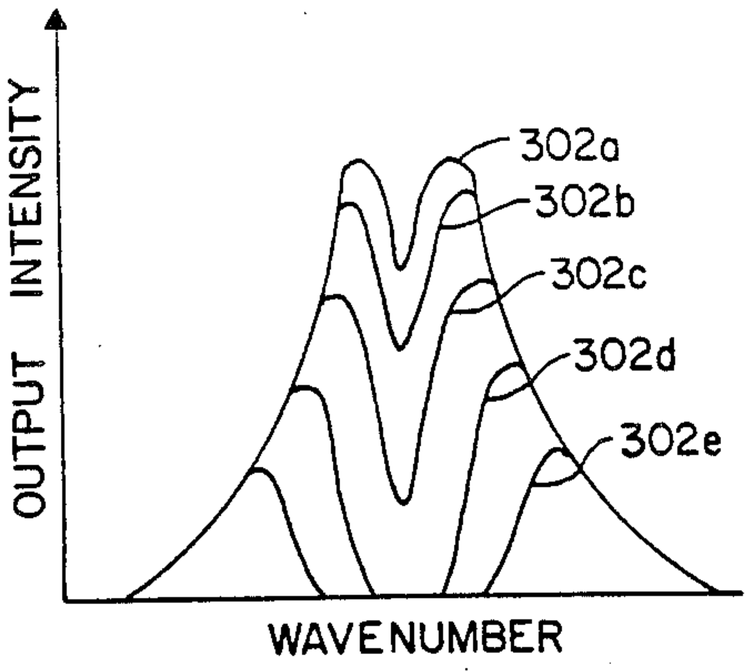


FIG. 10E

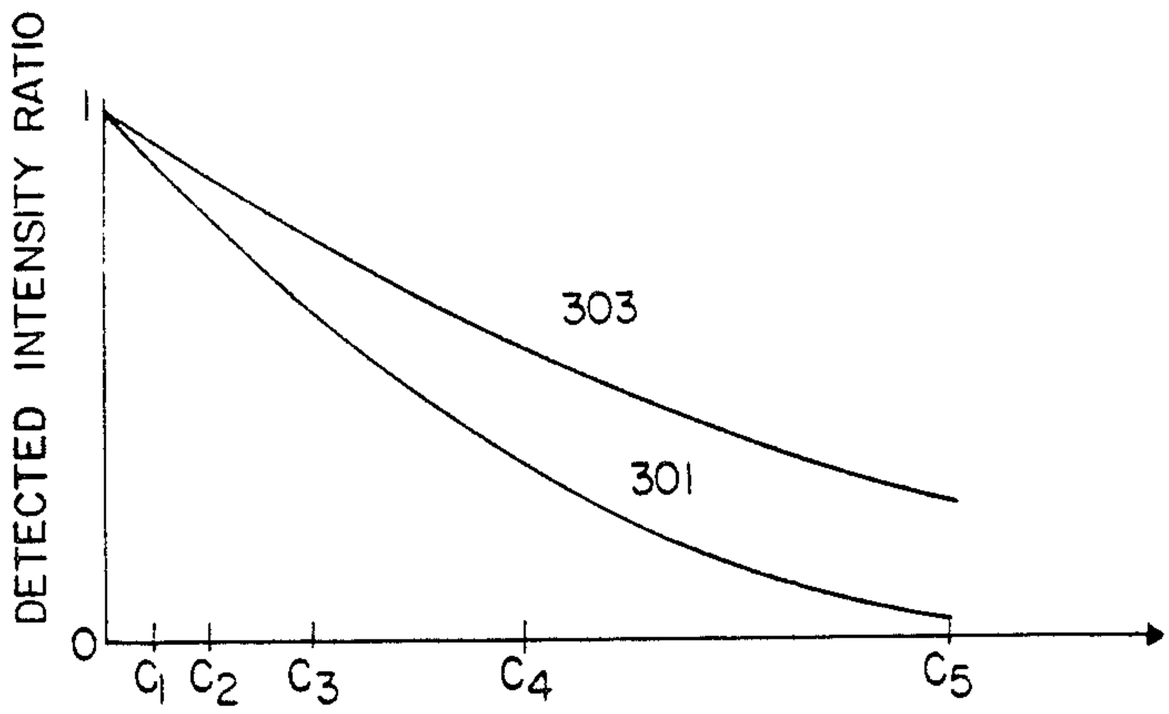

DETECTED INTENSITY RATIO
1
0
303
301
C1
C2
C3
C4
C5
RELATIVE CONCENTRATION

FIG. 10F

INFRARED MOLECULAR SPECIES MONITOR

FIELD OF INVENTION

This invention relates to an infrared gas phase molecular species monitor and in particular to a monitor which measures the absorption by a gas sample of at least one line of the emission source spectrum of the molecular species being monitored as a function of the concentration of the species in the gas sample.

BACKGROUND OF INVENTION

Techniques such as infrared absorption are currently employed to monitor gas phase molecular species such as hydrogen chloride (HCl) present in samples of the atmosphere or other gases. Typically, in such systems a broad band of infrared radiation is introduced into the gas sample. Because the molecular species in the sample tend to absorb some of that radiation in characteristic wavelength bands, the resultant reduction in the intensity of the infrared output signal in these bands is measured and used to determine the presence and concentration of the species in the sample.

Conventional infrared absorption systems exhibit a number of disadvantages. The absorption bands of various species are often close to one another, or overlap, and as a result it is typically difficult to distinguish the species being monitored from those having similar absorption bands.

Also it is sometimes difficult to achieve satisfactory sensitivity using the above method. This occurs for molecular species where the average spacing of the absorption lines is significantly larger than the average width of the lines. In these instances only a small fraction of the total broad band radiation will be absorbed within the molecular absorption lines. Accurately measuring low concentrations and small changes in concentration is particularly troublesome. As a result, in order to achieve enhanced absorption and improved sensitivity present monitors have utilized fairly long path lengths and complex multiple reflection optical units. This has added to the size and expense of the detection procedure and has made many infrared systems very inconvenient to transport and use in the field. These instruments also require constant supervision by expert operators.

SUMMARY OF INVENTION

It is therefore an object of this invention to provide an improved infrared monitor for measuring the presence of one or more gas phase molecular species.

It is a further object of this invention to provide such an improved infrared molecular species monitor having enhanced sensitivity particularly at low species concentrations.

It is a further object of this invention to provide an improved infrared molecular species monitor with improved differentiation between the species of interest and other species having absorption lines in the same spectral region.

It is a further object of this invention to provide an infrared gas phase molecular species monitor with improved resolution of high concentrations.

It is a further object of this invention to provide such an improved infrared monitor which is relatively simple, compact and inexpensive.

It is a further object of this invention to provide such an improved infrared monitor which may be conveniently transported and installed in the field.

It is a further object of this invention to provide such an improved infrared monitor which requires minimal operator attention.

This invention results from a realization that enhanced sensitivity and selectivity may be achieved in an infrared gas phase molecular species monitor by employing an infrared emission source which provides an emission spectrum of the molecular species to be monitored and measuring the absorption, by a gas sample, of at least one line of the emission spectrum as a function of the concentration of the molecular species in the gas sample.

This invention features an infrared monitor for measuring the presence of at least one gas phase molecular species which includes a sample path for containing a sample to be monitored for the molecular species. There are means for providing to the sample path a sample beam of infrared source emission of the molecular species to be monitored including at least one primary spectral emission line which is significantly absorbed by the molecular species for passage through the sample path. There are means for detecting the decrease in the intensity of the at least one primary infrared source spectral emission line passed through the sample as a function of the absorption of the at least one line by the molecular species present in the sample.

In a preferred embodiment the sample beam includes at least one secondary spectral emission line which is not significantly absorbed by the molecular species and the means for detecting includes means for sensing the output intensity of the at least one primary spectral emission line passed through the sample path and the output intensity of the at least one secondary spectral line passed through the sample path. The means for sensing may include a single detector. The means for detecting may further include means, responsive to the means for sensing, for comparing the output intensity of the at least one primary emission line and the output intensity of the at least one secondary emission line and means, responsive to the means for comparing, may be provided for determining the concentration of the molecular species in the sample. The means for comparing may include means for dividing one of the primary and secondary emission line intensities by the other. The means for detecting may also include means for selectively sensing the output intensities of the primary and secondary emission lines of the sample beam of radiation from the sample path and the intensities of a reference beam of the radiation in the primary and secondary emission lines. Means, responsive to the means for selectively sensing may be provided for normalizing the sensed output intensity of one of the primary and secondary emission lines of the sample beam with respect to the other. There may also be provided means, responsive to the means for selectively sensing, for normalizing the sensed intensity of one of the primary and secondary emission lines of the reference beam with respect to the other. The means for comparing may include means for comparing the normalized output intensity and the normalized reference intensity. The means for selectively sensing may include a single detector.

The means for selectively sensing may also include means for selectively transmitting the primary and secondary spectral emission lines in the sample beam and

the reference beam. Such means for selectively transmitting may include chopper means having first filter means for transmitting the at least one primary emission line and second filter means for transmitting the at least one secondary emission line and means may be provided for driving the chopper means to pass the first and second filter means selectively through the sample and reference beams of infrared radiation. Sensor means may be provided for sensing the location of chopper means.

The means for normalizing the sensed output intensity of one of the primary and secondary emission lines of the sample beam with respect to the other may include means for dividing one of the sensed output intensities by the other. The means for normalizing the sensed intensity in one of the primary and secondary emission lines of the reference beam with respect to the other may include means for dividing one of the sensed intensities by the other. The means for comparing the normalized sample beam intensities and the normalized reference beam intensities may include means for dividing one of the normalized intensities by the other.

The means for determining preferably includes means for calculating the concentration of the molecular species in the sample. Alternatively it may include means for retrieving a stored predetermined concentration of the molecular species corresponding to the comparison parameter of the primary and secondary emission line intensities. The means for determining may also include a stored predetermined concentration value of the molecular species corresponding to the comparison parameter of the normalized sample and normalized reference beam intensities.

The sample path may include an optical cell for containing the sample to be monitored for the molecular species. A combination of molecular species may be included in the sample path.

DISCLOSURE OF PREFERRED EMBODIMENT

Other objects, features and advantages will occur from the following description of a preferred embodiment and the accompanying drawings, in which:

FIG. **1** is a schematic view of an infrared gas phase molecular species monitor according to this invention;

FIG. **2** is a simplified axonometric view of the chopper wheel and the sample and reference beams of infrared radiation.

FIG. **3** is a graph illustrating the detecting output and reference (emission line) intensities versus the position of the chopper in FIG. **1**;

FIG. **4** is a cross sectional view of a preferred infrared emission source;

FIG. **5A** illustrates representative primary and secondary emission lines from an HCl emission source;

FIG. **5B** illustrates a representative transmission spectrum for the representative primary and secondary emission lines of HCl;

FIG. **5C** illustrates a representative output intensity at the detector of FIG. **1**;

FIG. **6** is a schematic view of a signal processor for normalizing and comparing the sensed detecotr intensities and for determining the molecular species concentration and a circuit for sensing the location of the chopper device;

FIG. **7** illustrates the variation in the measured concentration of HCl under ambient sea level conditions with variation in the ratio of the normalized detector intensities.

FIG. **8** is a flow chart for one method of resolving the proportion of molecular species in the sample gas;

FIG. **9** is a schematic diagram of a preferred alternative signal processor which digitally processes the detected intensity signals to determine the proportion of molecular species in the gas sample;

FIG. **10A** illustrates a relatively narrow primary emission line for an infrared molecular species emission source;

FIG. **10B** illustrates a wider primary emission line resulting from, for example, an increased concentration of HCl;

FIG. **10C** illustrates at increasing respective sample concentrations the absorption lines corresponding to the emission line of FIGS. **10A** and **10B** for a sample containing the molecular species being monitored;

FIG. **10D** illustrates the respective output intensities of the primary emission line of FIG. **10A** after it passes through samples having the molecular species concentrations of FIG. **10C**;

FIG. **10E** illustrates the respective output intensities of the primary emission line of FIG. **10B** after it passes through samples having the molecular species concentrations of FIG. **10C**;

FIG. **10F** illustrates for FIGS. **10D** and **10E** the variation in output intensity with variation in concentration; and

An infrared monitor for measuring the presence of a gas phase molecular species according to this invention may be accomplished by providing a sample path for containing a sample to be monitored for the molecular species. Typically, the sample path includes an optical cell. Although a multiple reflection optical cell such as a White cell may be employed, the monitor could operate using a cell which provides only a single reflection or no reflections whatsoever. A gas is introduced to and removed from the sample path so that the sample may be monitored for presence of, for example, HCl, H_2O vapor, hydrocarbons NO_2, NO_3, CO, CO_2 or other gas phase molecular species either alone or in combination.

A sample beam of infrared source emission of the molecular species to be monitored is directed through the sample path. The sample beam includes at least one primary, e.g., absorbing, spectral emission line which is significantly absorbed by the molecular species. A preferred infrared emission source includes a closed container or cell having at least one window for containing the molecular species to be monitored and means for heating the molecular species within the container sufficiently to cause that species to emit its characteristic infrared emission spectrum through the window of the container. It should be understood that although purely the molecular species of interest may be present in the emission source, more often that molecular species is united with and diluted by a relatively inert gas such as argon or nitrogen which does not emit radiation that is significantly absorbed in the spectral regions of interest. A preferred emission source container includes very thin (e.g., approximately 0.5 mm) windows composed of water-free quartz or sapphire having a low emissivity to reduce the emission of a continuum broad band of infrared radiation. The molecular species within the cell is heated by wire wound about the emission cell. The wire may be composed of an iron-chromium-aluminum-cesium alloy or other comparable material and typically is resistively heated by current from a battery or small generator. The emission cell and heater element are typically mounted within a housing which may be con-

structed of black anodized aluminum having exterior cooling fins to dissipate heat generated by the emission source. To further regulate heat loss from the emission source, insulation, such as ceramic fiber or similar material may be provided between the container and the housing. One or more openings are provided through the insulation and the housing to transmit the infrared radiation emitted by the heated gas within the container. To prevent excessive convective heat loss this opening may be covered by an insulating window composed of sapphire or a similar material with low emmissivity. The wire heater may be mounted to the inner surface of the ceramic insulation by a potting compound or equivalent means.

The decrease in the intensity of one or more of the absorbing infrared source spectral emission lines passed through the sample path is detected as a function of the absorption of those lines by the molecular species present in the sample. The level of such absorption is similarly a function of the presence and concentration of the molecular species in the sample. In a preferred device the decrease in intensity is determined as follows. The sample beam includes at least one secondary, e.g. nonabsorbing, spectral emission line which is not significantly absorbed by the molecular species. Although the terms absorbing and nonabsorbing are used herein it should be understood that emission in these regions are not totally absorbed or nonabsorbed. Rather, as is standard practice in the art, absorbing indicates that the emission is significantly absorbed whereas nonabsorbing indicates that the region is not significantly absorbed.

Means are provided for sensing the output intensity of the one or more absorbing infrared source spectral emission lines and, separately, the output intensity of one or more of the nonabsorbing emission lines passed through the sample path. It is preferred that a single detector be used to sense both of these intensities although in alternative embodiments separate detectors may be utilized for the absorbing and nonabsorbing emission lines. The output intensity of the one or more absorbing spectral lines and the output intensity of the one or more nonabsorbing spectral lines are compared such as by division or subtraction to provide a signal which is processed, for example, by a microprocessor to determine the concentration of the molecular species in the sample. That concentration may then be indicated by a printout, an LED display, or other appropriate means.

Instrument drift can occur when filters, which are used to transmit the absorbing and nonabsorbing emission lines, collect dirt or otherwise become contaminated at different rates, or when the detector spectral response changes. As a result the compared values may change despite no change in the concentration of the molecular species and erroneous measurements may be taken. To overcome this difficulty preferred embodiments of this invention employ means for selectively sensing the output intensities of the absorbing and nonabsorbing emission lines of both the sample beam and a reference beam of the infrared radiation. The reference beam does not pass through the gas sample. Again, a single detector is preferred for selectively sensing these intensities although multiple detectors may also be employed. The selective sensing is typically accomplished with a chopper or other means for selectively transmitting the absorbing and nonabsorbing emission lines of the sample and reference beams. Although a separate chopper may be employed for each beam, it is preferred that a single chopper device having first and second filters be used for both beams. The chopper is driven to pass the first and second filters selectively through the sample and reference beams of radiation. For example, the chopper device may include a rotating disk with narrow band filters spaced apart. Although 180° is preferred, alternative spacings may be employed. In monitoring a gas sample for the presence of HCl, desirable absorbing emission lines, i.e., lines which are significantly absorbed are centered at approximately 2795 and 2820 cm^{-1} and a preferred nonabsorbing spectral line is centered at approximately 2675 cm^{-1}. The sample beam may be chopped into alternating absorbing and nonabsorbing lines prior to introduction to the optical path. Alternatively, the first and second filters of the chopper device are driven through the output beam from the sample path. Typically, a lead selenide detector or other suitable photodetector is employed for detecting the sample output and reference beam intensities.

The output intensity of the one or more absorbing spectral lines of the sample beam is divided by, subtracted from or otherwise normalized with respect to the output intensity of the one or more nonabsorbing spectral lines of the sample beam. Similarly, the sensed intensity of the one or more absorbing spectral lines of the reference beam is divided by, subtracted from or otherwise normalized with respect to the sensed intensity of the nonabsorbing spectral lines of the reference beam. The normalized sample beam intensity and normalized reference beam intensity are then compared by division, subtraction or otherwise and a signal representative of this comparison parameter is used to determine the amount of molecular species in the sample. The amount of molecular species may be calculated from the compared value. Alternatively, the comparison parameter may be used to retrieve from a memory a corresponding value of the molecular species. A sensor may be provided for sensing the location of the chopper so that the detected intensities may be processed in the proper sequence. Alternatively, where the filters are spaced at intervals other than 180°, a sensor may not be required.

The temperature and/or pressure of the sample gas may also be sensed and used by a retrieval or calculation circuit in determining the amount of the trace element in the sample at the sensed temperature and/or pressure. The determined amount may be indicated by, for example, a dial or a readout, and if the molecular species exceeds a predetermined amount, an audio or visual alarm may be activated.

By dividing or otherwise comparing the normalized intensity of the sample beam with a normalized intensity of the reference beam the present invention overcomes the problem of detector drift. If, the filter which transmits the nonabsorbing spectral lines collects dirt or otherwise becomes contaminated at a rate different than the filter which transmits the absorbing spectral lines, the resulting changes in the normalized intensity of the absorbing and nonabsorbing spectral lines are exhibited by both the sample beam and the reference beam. Therefore, the compared value remains constant and the system remains calibrated.

In alternative embodiments the amount by which the primary emission lines are absorbed, and hence the concentration of the molecular species being monitored, may be determined by comparing the output

intensity of the one or more absorbing emission lines directly with the sensed intensity of these lines in a reference beam of the infrared source emission.

There is shown in FIG. **1** an infrared monitor **10** according to this invention which includes an optical cell **12** into which is introduced a sample gas is from source **14** to be monitored for one or a combination of molecular species of interest. When the monitoring of the sample gas has been accomplished as described below the gas is discharged from the cell as indicated by arrow **16**. The flow of sample gas **15** into and out of optical cell **12** may be either periodic or continuous. Cell **12** may include a multiple reflection optical cell such as a White cell or an optical cell employing only a single reflection or a single pass with no reflections whatsoever.

Infrared emission source **18** provides an infrared source emission **20** of the molecular species to be monitored. Emission **20** includes one or more primary or absorbing emission lines which are significantly absorbed by the molecular species being monitored in the sample gas and at least one secondary or nonabsorbing emission line which is not significantly absorbed by the molecular species. Emission **20** is split by beam splitter **22** into a sample beam **24** and a reference beam **26**. Sample beam **24** is directed by beam splitter **22** and reference beam **26** is directed by beam splitter **22** and mirror **28** toward chopper wheel **30**.

The chopper wheel, further shown in FIG. **2**, is rotatable about an axis **32** and selectively transmits both sample beam **24** and reference beam **26**. Chopper **30** includes a first filter **34** which transmits only the absorbing emission lines of infrared radiation and a second filter **36** which transmits only the nonabsorbing emission lines of the infrared radiation. Chopper wheel **30** is rotated in the direction of arrow **38** so that filters **34** and **36** are alternately passed through both sample beam **24** and reference beam **26**. For example, in FIG. **2** first filter **34** is shown passing through sample beam **24**. This causes the absorbing emission lines of infrared radiation to be transmitted through the filter. As indicated by arrow **24***a*, FIG. **1**, the sample beam is then directed by mirror **42** into optical cell **12** so that it passes through the sample gas **15** in cell **12**. After passing one or more times through the sample gas **15**, the absorbing emission lines exit cell **12** as beam **24***b* and are transmitted through a beam splitter **44** and their intensity A, FIG. **3**, is sensed by a detector **46**. While sample beam **24** is being transmitted through filter **34**, chopper wheel **30** blocks transmission of reference beam **26** and, as a result, the intensity of that beam is not measured.

The chopper wheel continues rotating in the direction of arrow **38**, FIG. **2**, and after one-quarter turn, i.e., at the 90° position, first filter **34** is at the position indicated in phantom. The absorbing emission lines of the reference beam **26** are then transmitted through filter **34**. The transmitted portion **26***a*, FIG. **1**, of the reference beam is reflected by beam splitter **44** and sensed by detector **46**. At the same time, transmission of sample beam **24** is blocked by chopper **30** and, as a result, only the intensity B, FIG. **3**, of the absorbing emission lines of the reference beam is measured.

An additional one-quarter turn of the chopper wheel to the 180° position places filter **36** in the path of sample beam **24**. Accordingly, the nonabsorbing emission line or lines of the sample beam are transmitted through the chopper and passed through optical cell **12**. The output intensity C, FIG. **3**, of the one or more nonabsorbing emission lines of the sample output beam **24***b*, FIG. **1**, is then sensed by detector **46**. Filter **36** is finally rotated through the path of reference beam **26** to the 270° position so that the intensity D of the nonabsorbing emission lines of the reference beam may be similarly detected.

With each revolution of chopper **30** detector **46** successively senses the intensities of the absorbing emission lines and the nonabsorbing emission lines of the sample output beam **24***b* and the reference beam **26***a*. Between each quarter turn the sample and reference beams are blocked by the chopper and no infrared intensity is detected.

Following detection of the four intensities A, B, C and D, those intensities may be displayed, for example, on an oscilloscope **50** and they are provided to a signal processor **52** where they are processed, as described more fully below, to determine the concentration of the molecular species in the gas sample.

Although chopper **30** is shown, in FIG. **1**, transmitting the sample beam before it is passed through optical cell **12** in alternative embodiments the chopper may be arranged after the cell and transmit sample output beam **24***b*. In addition, if source or filter drift can be tolerated then the reference beam **26** may be omitted. For example, source and detector drift could be compensated for by a third nonabsorbing band.

A preferred emission source **60** for providing the absorbing and nonabsorbing emission spectral lines while at the same time largely eliminating the broad band continuum infrared emission is shown in FIG. **4**. The emission source includes a housing **62** having a peripheral jacket **64** and end plates **66** and **68** which are secured to jacket **64** by screws **70**. An insulation member **72** is mounted within housing **62** and a central axial opening **73** is formed through housing **62** and insulation member **72**. A sealed container or emission cell **74** having end windows **76** is disposed longitudinally within opening **73** and is secured to insulation member **72** by potting compound **78**. In particular, emission cell **74** may include a projection **80** which is formed when cell **74** is blown or otherwise constructed. The emission cell contains the gas phase molecular species being monitored plus a relatively inert gas which does not emit infrared radiation in the wavelength regions absorbed by the sample gas. For example, if gas sample **15** is being monitored for HCl, cell **74** may be filled, for example, to a pressure of one-third atmosphere with a mixture of nitrogen and HCl. A resistively heated wire heating element **82** is introduced through a ceramic feedthrough **84** into the housing. Element **82** extends through insulation member **72** and is embedded in potting compound **78** and disposed about emission cell **74**.

Emission source **60** is operated by employing a battery or generator or similar means, not shown, to energize heater element **82**. The molecular species within cell **74** is heated sufficiently by element **82**, for example to 1000° K, to emit its characteristic infrared emission spectral lines. This emission exits cell **74** through windows **76** and exits emission source **60** through opening **73**. The emission source is held by a support structure, not shown, and is arranged with opening **73** disposed vertically so that free convection does not excessively cool the lower window **76** of cell **74**. The upwardly emitted infrared radiation **20** is redirected by a mirror **79** and split into reference and sample beams as described in connection with FIGS. **1** and **2**. At the same time, the downwardly emitted radiation **20***a* is directed

by a mirror **79***a* away from the optical path of emission **20**.

Emission source **60** includes a number of features which permit its temperature to be maintained at a substantially constant level. For example, cooling fins **86** are provided on the exterior of jacket **64** so that heat is dissipated uniformly from the emission source. Housing **62** is also constructed from a material such as black anodized aluminum which efficiently dissipates the heat generated by heater element **84**. On the other hand, insulation member **72** prevents the heat from being dissipated too rapidly from the emission source and helps maintain the temperature at a substantially constant level. Convective heat loss through opening **73** is further reduced by an insulating window **90** which is mounted over the top of opening **73** and held in place by a retainer **92** attached to jacket **64** by screws **70**. Because only a small portion of the surface area of cell **74** is exposed, i.e., windows **76**, radiative losses from cell **74** are minimized; yet an effective aperture for the radiation is provided through opening **73**. Both the window **76** and window **90** are composed of a low emissivity substance such as quartz or sapphire. This greatly reduces the intensity of the continuum infrared spectrum which may be emitted by these elements. As a result, substantially all of radiation **20** consists of the infrared spectral emission lines of the molecular species within cell **74**.

Because detector **46**, FIG. **1**, is detecting the intensity of only the infrared source spectral emission lines, and not a broad band continuum of infrared radiation, measuring the absorption of the infrared emission by the molecular species in question is facilitated. As shown in FIG. **5A** where the molecular species of concern is HCl, beam **20** includes absorbing emission lines **100** centered on the wave numbers 2795 and 2820 cm^{-1} respectively. The sample beam also includes a nonabsorbing emission line **102** centered on the wave number 2675 cm^{-1}. Additional emission lines are not shown for clarity. These spectral lines are transmitted in both sample beam **24** and reference beam **26** of FIG. **1**. However, when chopper **30** passes filter **34** through beam **24** only lines **100** are passed through to the optical cell. Conversely, when filter **36** is passed through the sample beam, only line **102** passes through to the optical cell. Similarly, lines **100** and line **102** are selectively transmitted as the reference beam **26** engages the respective filters of the chopper.

As emission lines **100** and **102** alternately pass through the gas in the optical cell their intensity is reduced to the extent that the emission lines are absorbed by the molecular species (HCl) present in the gas sample. As indicated by absorption lines **104**, FIG. **5B**, the molecular species in the sample significantly absorbs infrared radiation which corresponds in wavelength to the absorbing emission lines passed through the gas. The size of lines **104** varies according to the amount of molecular species in the sample. As further indicated by absorption line **106** the HCl in the sample does not substantially absorb radiation corresponding in wavelength to the nonabsorbing emission line **102**. As a result of the absorption of the absorbing emission lines **100** by the molecular species in the gas sample, intensity of the output absorbing emission lines **100***a*, FIG. **5C**, is significantly reduced. Whereas the absorbing emission lines provide an intensity signal B (e.g., the reference intensity), prior to introduction to the optical cell, their output intensity is reduced to A. At the same time because nonabsorbing emission line **102** is absorbed by only an insignificant amount, the intensity of the nonabsorbing emission line **102***b* which exits the optical cell is reduced only slightly from D to C. By detecting the decrease in the intensity of the absorbing emission lines the level of absorption by the molecular species being tested and, hence, the concentration of that species in the sample can be determined as described more fully below.

In contrast to the system of this invention, when a broad band continuum infrared source is employed, a broad band **103**, FIG. **5A**, is absorbed to the extent of absorption lines **104**, FIG. **5B** and the intensity of its output signal **103***a*, FIG. **5C**, remains relatively large compared to that of the initial signal **103**. As a result, the decrease in intensity, and hence the absorption and concentration of the molecular species in the sample, are quite difficult to monitor, particularly at low concentrations where the intensity decrease may be negligible. Moreover, species other than the species being monitored may absorb a portion of the broadband sample beam and as a result provide misleading indications of absorption and erroneous determinations of concentration. The present invention alleviates these difficulties: even small reductions in the intensity of absorbing lines **100** are detectable, being compared to a smaller emitted intensity, and absorption by irrelevant species with neighboring absorption lines is avoided.

A signal processor **52** for processing the detected intensity signals A, B, C and D is shown in FIG. **6**. The respective signals are provided from detector **46** to a switching circuit **121**. A sensor **122** detects appropriate indicia **125** disposed around the circumference of wheel **30** and provides a signal to circuit **121** which identifies the signal received from detector **46** as either signal A, B, C or D. The switching circuit feeds signals A and C, respectively representing the intensities of the absorbing and the nonabsorbing emission lines of the sample output beam **24***b*, to divider circuit **123** where they are divided to provide normalized signal A/C. Similarly, signals B and D, representing the intensities of the absorbing and nonabsorbing emission lines, respectively, of the reference beam are provided by switching circuit **121** to a divider circuit **124** where they are divided to yield the normalized signal B/D. Signals A/C and B/D are divided in a divider circuit **126** to yield signal R (e.g., $(A \times D/(B \times C))$. Signal R is provided along with signals indicative of the temperature T and the pressure P of the fluid of the sample to a table retrieval circuit **128** where the proportion of HCl or other molecular species being measured in the sample is retrieved from calibration curves, described more fully in connection with FIG. **7**, which are stored in the memory of the circuit. Alternatively, the proportion of molecular species in the gas sample may be determined by entering signal R into a calculation circuit **130** where a conventional algorithm is employed to calculate the proportion as described in connection with FIG. **8**. The determined concentration of the molecular species is indicated on a readout **132** and if the proportion reaches an undesirably high level, an alarm **134** is activated.

A sensor is not required if the filters are arranged on the chopper at an interval other than 180°. For example, if they are separated by 135°, signals A, B, C and D are provided at 0°, 90°, 135° and 225°, respectively. This uneven spacing serves to identify the respective signals and eliminates the need for a sensor.

The calibration curve, such as in FIG. **7**, may be used by table retrieval circuit **128** for determining stored HCl

concentration values. Values along the X axis represent the divider circuit output signal R provided to the retrieval circuit **128**. Values along the Y axis indicate the concentration of HCl in parts per million. These values are obtained in an HCl gas sample which is maintained at a constant temperature of 72° F. and pressure of one atmosphere. Similarly shaped curves, not shown, at different concentrations can be obtained at different temperatures and pressures. Each of these calibrated curves is compiled by employing a gas sample having known concentrations of HCl and predetermined temperatures and pressures and measuring values R for such samples.

Logic which may be employed in circuit **130** to calculate the proportion of trace element is shown in FIG. **8**. Table **191** is provided with known combinations of values of temperature T, pressure P, ratio R and X, where X, a function of T, P and R equals the log of the concentrations C. Table **191** thus expresses the functional dependence of X on T, P and R. Known temperatures, pressures and R values T_1, T_2, P_1, P_2 and R_1, R_2 which bound the detected values T', P' and R', respectively, are retrieved from Table **191**, step **192**. These values are used to perform known 3-dimensional linear interpolation, steps **193**, **194** and **195** to calculate the value of X which is associated with T', P' and R'. Concentration is calculated, step **196**, by re-exponentiating X and multiplying e^x by C_0 where C_0 is a typically constant predetermined scaling factor.

In an alternative preferred embodiment the intensity signals alternatively may be processed digitally as shown in FIG. **9**. Detector **46** is connected to a 100-volt bias supply **210** through a resistor **212**. Because the noise and sensitivity of detector **46** is strongly temperature dependent the detector includes a thermistor which provides a temperature signal t over line **214** and through amplifier **216** to microcontroller **218**. A thermocouple **220** measures the temperature of the incoming gas entering optical cell **12**. Its signal T proceeds over line **222** through thermocouple signal conditioner **223** and amplifier **224** to microcontroller **218**. A pressure transducer **228** detects the pressure of the incoming gas sample and provides a signal P representative of that pressure over line **230** and through amplifier **232** to the microcontroller.

The absorption signals A, B, C and D provided by detector **46** are amplified and buffered by a preamplifier **236** and then directed through an amplifier **238**, a sample and hold circuit **240** and an A/D converter **242**. The signals are then transmitted through digital data buffers **243**, **244** to the input of microcontroller **218**. As a result each signal A–D is converted to a respective, for example, fourteen bit digital signal AD, BD, CD, DD.

The microcontroller is programmed in a conventional manner to process the signals so that signal AD is normalized with respect to signal CD, signal BD is normalized with respect to signal DD and the normalized intensity signals are compared to provide a signal R, not shown. The steps of such a program may include, for example, the division steps performed by the divider circuits described in FIG. **6**. The signal R derived in this manner is then employed in either a table retrieval or a calculation in microcontroller **218**, which operate analogously to the description in FIGS. **7** and **8** to provide the detected proportion of trace element to display **132***a*. Alarm **134***a* sounds when the concentration exceeds a predetermined level.

In order to prevent the heat generated by motor **260** and the ambient environment from disrupting the concentration determination the detector may include and be cooled by a solid state heat pump **219**. Microcontroller **218** reads detector temperature t and feeds back a control signal C through buffer **245**, low pass filter **246** and power operational amplifier **248** which operates the heat pump when the detector temperature t is too high.

Again, the sample and reference beams of infrared radiation are chopped into their respective absorbing and nonabsorbing wavelength bands by a chopper wheel **30***a*. The wheel is driven by a motor **260** which is controlled by the microcontroller. Sensor **122***a* senses indicia **125***a* on the wheel and provides a signal to microcontroller **218** over line **264** which indicates to the microcontroller which signal AD–DD it is receiving.

The maximum resolvable concentration and sensitivity of the monitor may be adjusted by varying the size and shape of the primary emission lines. For example, as absorbing emission line **300**, FIG. **10A**, is passed through a gas sample in which the molecular species has a concentration of C_1, FIG. **10C**, emission line **300** is somewhat absorbed by the molecular species in the gas, e.g., absorption line C_1 reduces emission line **300**, and its resulting output intensity is **300***a*, FIG. **10D**. Passing emission line **300** through a sample having a larger concentration C_2, FIG. **10C**, of the molecular species results in an even smaller output intensity, **300***b*, FIG. **10D**. As the concentration of the molecular species increases the output intensity of the absorbing emission line becomes smaller until with a concentration of greater than C_3, e.g., with a concentration of C_4 or C_5, absorbing emission line **300** is almost entirely absorbed and the output intensity for the emission line at these concentrations is harder to detect. See the detected intensity ratio line **301**, FIG. **10F**. With the absorbing emission line of the intensity and width of line **300** it is therefore impossible to detect concentration differences between C_4 and C_5, indeed, to detect any higher levels of concentration.

To improve the concentration measurements at relatively high concentrations, it is advantageous to increase the concentration of the molecular species of interest in the emission source so that a broadened emission line **302**, FIG. **10B**, which corresponds to the position of line **300**, is provided. The line may also be broadened by similarly increasing the path length or by increasing the pressure, varying the temperature or changing the concentration of the diluting gas in the emission cell. As broadened line **302** is passed through a gas sample having a molecular species concentration of C_1, FIG. **10C**, the molecular species in the sample absorbs a portion of line **302** and an output intensity of **302***a*, FIG. **10E**, is provided. At each higher concentration level, e.g., C_2, C_3, C_4 and C_5, progressively more of emission line **302** is reduced as shown by curves **302***b–e*. However, even at the very high concentration level of C_5 a discernable output signal **302***e* is provided. As shown by line **303**, FIG. **10F**, the intensity signal does not drop to zero and measurements at very high concentrations can be made.

The disadvantage of employing a relatively wide signal lies in that it is not as sensitive as the narrow signal. For example, as shown by line **303** in FIG. **10F**, when a wide emission line **302** is used at very low concentrations (below C_1) there is a smaller change in the output intensity. As a result, it may become quite difficult to distinguish the increasingly smaller concentra-

tions from one another. On the other hand, employing the narrower absorbing emission line **300** of FIG. **10A** provides a significantly greater change, line **301**, in intensity as the concentration is reduced below C_1. Increasingly smaller concentrations can be distinguished and as a result, enhanced sensitivity is provided. Accordingly, narrow emission lines should be employed when such sensitivity is required.

In alternative embodiments the maximum resolvable concentration may be improved by utilizing a larger number of primary emission lines.

Although specific features of the invention are shown in some drawings and not others, this is for convenience only as each feature may be combined with any or all of the other features in accordance with the invention.

Other embodiments will occur to those skilled in the art and are within the following claims:

What is claimed is:

1. An infrared monitor for measuring the presence of at least one gas phase molecular species comprising:

a sample path for containing a sample to be monitored for the molecular species;

means for providing to said sample path a sample beam of an infrared source of emission spectrum of the molecular species to be monitored including at least one primary emission line which is significantly absorbed by the molecular species and at least one secondary emission line which is not significantly absorbed by the molecular species for passage through said sample path;

means for selectively sensing the output intensities of said primary and secondary emission lines of said sample beam of radiation from said sample path and the intensities of said primary and secondary emission lines in a reference beam of said radiation;

means, responsive to said means for selectively sensing, for normalizing the sensed output intensity of the sample beam of radiation in one of said primary and secondary emission lines with respect to the other;

means, responsive to said means for selectively sensing, for normalizing the sensed output intensity of the reference beam of radiation in one of said primary and secondary emission lines with respect to one another; and

means for comparing the normalized sample beam intensity and the normalized reference beam intensity.

2. The infrared monitor of claim **1** in which said means for selectively sensing includes a single detector.

3. The infrared monitor of claim **1** in which said means for selectively sensing includes means for selectively transmitting said primary and secondary spectral emission lines in said sample beam and said reference beam.

4. The infrared monitor of claim **3** in which said means for selectively transmitting includes chopper means having first filter means for transmitting said at least one primary emission line and second filter means for transmitting said at least one secondary emission line and means for driving said chopper means to pass said first and second filter means selectively through said sample and reference beams of infrared radiation.

5. The infrared monitor of claim **4** further including sensor means for sensing the location of said chopper means.

6. The infrared monitor of claim **1** in which said means for normalizing the sensed output intensity of one of said primary and secondary emission lines of the sample beam with respect to the other includes means for dividing one of the sensed output intensities by the other.

7. The infrared monitor of claim **1** in which said means for normalizing the sensed intensity of one of said primary and secondary emission lines of the reference beam with respect to the other includes means for dividing one of the sensed intensities by the other.

8. The infrared monitor of claim **1** in which said means for comparing the normalized sample beam intensity and the normalized reference intensity includes means for dividing one of the normalized intensities by the other.

9. The infrared monitor of claim **1** in which said means for detecting including means for retrieving a stored predetermined concentration value of the molecular species corresponding to the comparison parameter of the normalized sample beam and normalized reference beam intensities.

10. The infrared monitor of claim **1**, in which said means for detecting further includes means for calculating the concentration of the molecular species in the sample.

11. An infrared monitor for measuring the presence of at least one gas phase molecular species comprising:

a sample path for containing a sample to be monitored for the molecular species;

means for providing to said sample path a sample beam of an infrared source emission spectrum of the molecular species to be monitored including at least one primary emission line which is significantly absorbed by the molecular species and at least one secondary emission line which is not significantly absorbed by the molecular species for passage through said sample path;

means for selectively sensing the output intensities of said primary and secondary emission lines of said sample beam of radiation from said sample path and the intensities of said primary and secondary emission lines in a reference beam of said radiation;

means, responsive to said means for selectively sensing, for normalizing the sensed output intensity of the sample beam in one of said primary and secondary emission lines with respect to the other;

means, responsive to said means for selectively sensing, for normalizing the sensed intensity of the reference beam of radiation in one of said primary and secondary emission lines with respect to the other;

means for comparing the normalized sample beam intensity and the normalized reference beam intensity; and,

means, responsive to said means for comparing, for determining the concentration of molecular species in the sample.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 4,782,232

DATED : November 1, 1988

INVENTOR(S) : Bernstein et al

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 1, between lines 2 and 4, insert the following:

--The invention was made with Governmental support under F04704-84-C-0312 awarded by the Department of Defense. The Government has certain rights in the invention.--

Signed and Sealed this

Eighteenth Day of February, 1992

Attest:

HARRY F. MANBECK, JR.

Attesting Officer

Commissioner of Patents and Trademarks